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DYNAMIC MECHANICAL MEASUREMENT OF POLYPHENYLSULFONE (RADEL)

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Interim Technical Report

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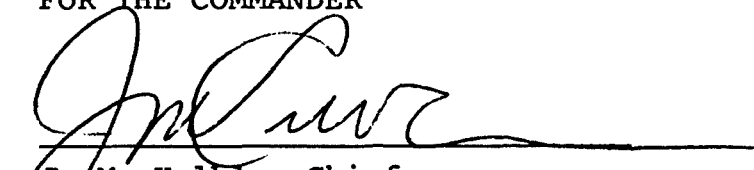
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temperature was characterized by Parallel Plates measurement and a maximum similar to the liquid-liquid transition was observed. Viscosity in this region was also measured as a function of frequencies. A Master Curve was constructed from the Torsion and Parallel Plates data, and the frequency shift parameters were fitted to the WLF equation.

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FOREWORD

This interim report was prepared by the University of Dayton Research Institute, Dayton, Ohio under United States Air Force Contract F33615-78-C-5126, Dr. D. R. Wiff, Principal Investigator. Co-authors were Dr. C. Y. Lee, Mr. J. D. Henes, and Mr. T. E. Grossman, University of Dayton, Research Institute.

This contract was initiated under Project No. 2419, Dr. F. E. Arnold, project scientist, Polymer Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio.

This report covers research conducted from July 1978 to December 1978.

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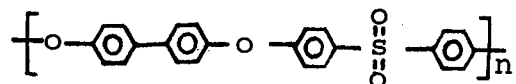
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SECTION I

INTRODUCTION

At the present time, polyphenylsulfone (Radel)



and acetylene terminated sulfone (ATS) are being considered as a possible system for the reactive plasticizer program. This program emphasizes a low processing temperature and a high use temperature. It uses the processing technology of thermoplastics and the mechanical properties of thermosets. It is expected that the mechanical properties of the various percentage blends will be measured and evaluated in the future. Information about the mechanical properties of Radel itself will be helpful in interpreting the future blend results. Interest has been expressed by workers in the Composite and Adhesives Branch of AFML to obtain viscosity information about Radel at high temperatures for use in processing composites. In light of these needs, the dynamic mechanical properties of Radel are characterized in this work from -150°C to 380°C . The two sub- T_g transitions of the material are characterized and their energies of activation are evaluated through the temperature frequency shifts of the transition maxima.

Another purpose of this investigation is to evaluate the different modes of operation available for bulk samples with the newly acquired Rheometrics Mechanical Spectrometer (RMS). RMS can measure both the tensile and torsional properties of bulk polymer specimens. Among the modes included in this report are torsional bar, tensile film, 3-point bending, and parallel plates. The Parallel Plates experiment is for measurements above the T_g region. In the past, materials in bulk form were characterized in this laboratory with the Rheovibron dynamic viscoelastometer. Results obtained with the RMS will be compared with those obtained with the Rheovibron.

Mechanical properties of polymeric materials are highly dependent upon the mode of measurement. The result (modulus, compliance, or viscosity) obtained from a measurement is the response of the material to a certain specific perturbation. This response is the manifestation of the intrinsic properties of the material, namely, the retardation spectrum or the relaxation spectrum. It has been generally accepted that these spectra are the desirable characterization of polymeric materials near the T_g region since the information is explicitly independent of the experimental conditions. However, these spectra can only be obtained through the construction of a master curve utilizing both temperature and frequency variations and then mathematically transforming the master curve.⁽¹⁾ Both tasks are difficult because the master curve construction requires tedious experimental procedures, and the transformation is mathematically ill-posed. The transformation difficulty has been improved through the regularization method.⁽²⁾ Because of the temperature control and frequency sweep capability of the RMS, master curves can be constructed with relative ease. A master curve will be constructed in this report with the Radel results, and the two constants in the Williams, Landel and Ferry⁽¹⁾ (WLF) equation will be evaluated. The result can be used later for further development of the regularization method.

This work can also be considered as a preliminary part of the broader chemical structure - mechanical properties correlation program. To facilitate such a correlation, information about the mechanical properties of structurally known polymers is needed. The results of this work is an initial step in this direction.

SECTION II

EXPERIMENTAL

For the Rheovibron measurements, a test specimen was cut from a 10 mil film cast by Union Carbide. The Parallel Plates specimen was made by stacking four 10 mil films together. These were then fused into one piece by subjecting them to a high temperature (220°C) treatment under pressure (~ 900 kg) for five hours. Then a 2.5 cm diameter disc test specimen was cut out of this fused film by use of a punch.

The test specimens for all other measurements were hot molded from powder. The rectangular bar sample was prepared by placing Radel powder in 110°C vacuum oven for a day. The mold was prepared by spraying each piece of the disassembled mold with Frekote 33, an interface releasing agent, and then the mold was assembled. Next the mold was heated to approximately 115°C and held at that temperature about 30 minutes. The Radel powder was hand packed into the mold and the open mold was placed back into the press. The thermostats on the press were then set between 290°C and 340°C , and it takes approximately 15 minutes for the mold to reach the set temperature. After the sample was at the set temperature for approximately one hour, the mold was closed and about 2700 kg of pressure was applied to the mold. Then the heater on the press was turned off and the mold was allowed to cool. The torsional and 3-point bending specimens made in this manner are rectangular bars of the dimensions of about $0.34 \times 1.27 \times 6.40$ cm. The tensile specimen was film of about 20 mil thickness.

The pertinent test specimen geometries and the equations of calculation for different modes on the RMS used in this report are reproduced in the Appendix.

All measurements were made in the temperature-frequency sweep mode. The temperature of the environmental chamber where the tested specimen was housed was adjusted to a constant value.

After a predetermined time delay, the measurement was initiated by a pulse from the temperature control unit to the Rheophaser, the measurement control unit. The measurement covered a three decade frequency range. Starting from 0.1 rad/sec (16 mHz), frequency was increased stepwise in log scale up to 100 rad/sec (16 Hz). At the end of the frequency sweep, a pulse was returned to the temperature control unit to increase the controlled temperature by a predetermined amount and the cycle was repeated. The strains applied to the test specimen were kept within 0.5% to insure the measurements were in linear range in all cases except the Parallel Plates measurement, where the strain was 8%.

SECTION III

RESULTS AND DISCUSSION

TORSION

The dynamic mechanical properties of Radel were measured under the torsional mode from -150° to 265°C . The experiment was stopped shortly after the major transition because Radel has a very short rubbery plateau. At 265°C the material is already in the flow region. Thus, not only is the sensitivity of the instrument a problem, but difficulties are also experienced in maintaining proper tension on the specimen.

Figure 1 shows the G' , G'' , and $\tan \delta$ of Radel obtained with the RMS at $\omega = 10.0$ rad/sec. Similar plots have been obtained with other frequencies ranging from 0.1 rad/sec to 100 rad/sec. All plots show similar structure except the maxima of the G'' and $\tan \delta$ peaks are occurring at different temperatures. The frequency vs. temperature effect will be discussed in a later section. The result agrees well with the mechanical properties plot of Radel provided by Union Carbide⁽¹¹⁾, which shows a major glassy (γ) transition at about -110°C (with $\tan \delta$ maximum value of 0.028) and a minor peak (β) at 45°C (with $\tan \delta$ maximum of about 0.015). The frequency used in the Union Carbide result was not given. The Union Carbide result also shows a shear modulus of $\sim 7 \times 10^9$ dynes/cm² around room temperature as compared with a value of 7.7×10^9 dynes/cm² at 20°C in the RMS result.

The Rheovibron result for Radel at ($\omega = 69$ rad/sec or cycle/sec) shows only one detectable glassy state transition (Figure 2). The small peak (the β transition) at about room temperature was not detected. It is possible that the magnitude of the small transition peak is slightly smaller than the resolution of the instrument. This argument however is debatable, since both the RMS data and the Union Carbide data indicate that the β transition maximum is about one half the value of the γ transition maximum which on Figure 2 should be just above the limit of the instrument's

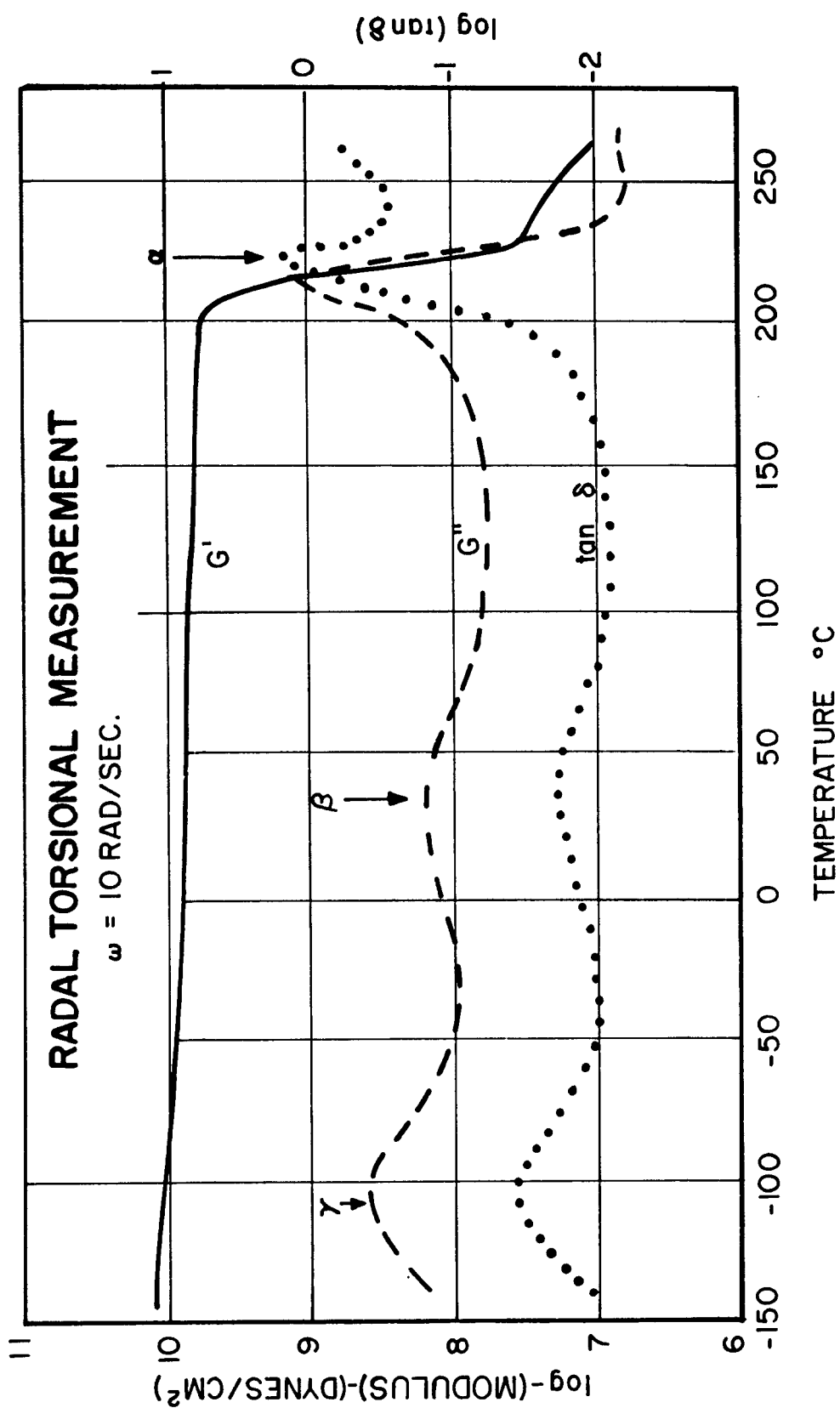


Figure 1. Rectangular Torsion Result (G' , G'' and $\tan \delta$) as a Function of Temperature ($\omega = 10 \text{ rad/sec}$).

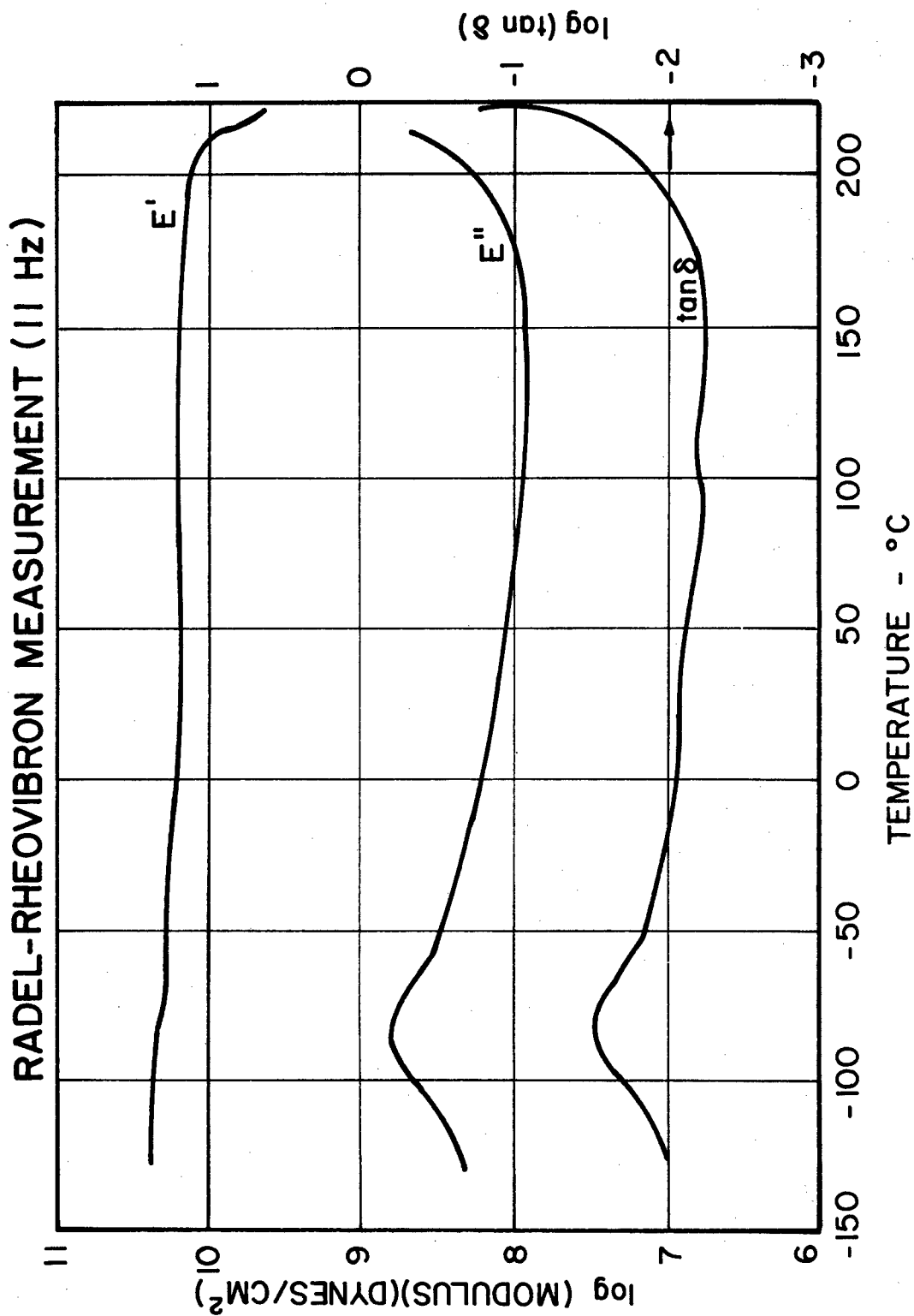


Figure 2. Rheovibron Result (E' , E'' and $\tan \delta$) as a Function of Temperature at 11 Hz.

resolution. This point is further complicated by the fact that similar characteristics are observed in the tensile and 3 point-bending experiments (see below).

TENSILE AND 3 POINT-BENDING

The tensile experiment was performed with a film specimen while the 3 point-bending was with a rectangular bar. Figure 3 shows the results from these experiments at 10 rad/sec. In these experiments, the resultant force being measured is in the same direction as the tension applied on the specimen to keep it from warping; so the problem faced in the torsional experiment at temperatures above T_g is more acute in these cases. As a result, the data shown in Figure 3 do not go much past the T_g . In the case of tensile measurement, this problem can be slightly alleviated by setting the tension shortly before the measurement is taken and using smaller oscillation amplitude together with longer integration time. Figure 4 shows how these adjustments together can improve the situation and data were obtained into the flow region. However these data should be regarded with caution because polymer samples do show tension relaxation which when added on top of the dynamic response force will make the dynamic signal look as if it is having a baseline drift. The Rheophaser will analyze the composite signal and mistakenly take the relaxation effect as a phase shift. Below T_g the relaxation effect is usually too small in the time scale of the frequency cycle time, so relaxation effect is not so much of a problem. Room temperature fluctuation can also cause a baseline drift in the electronics, although this effect on the result is not as prominent as the relaxation. The baseline drift problem is also encountered in torsional experiments.

Another problem with the tensile mode is the fact that the input signal to the Rheophaser is a composite of the transient force that keeps the specimen under proper tension and the dynamic force. The transient force is usually large in comparison

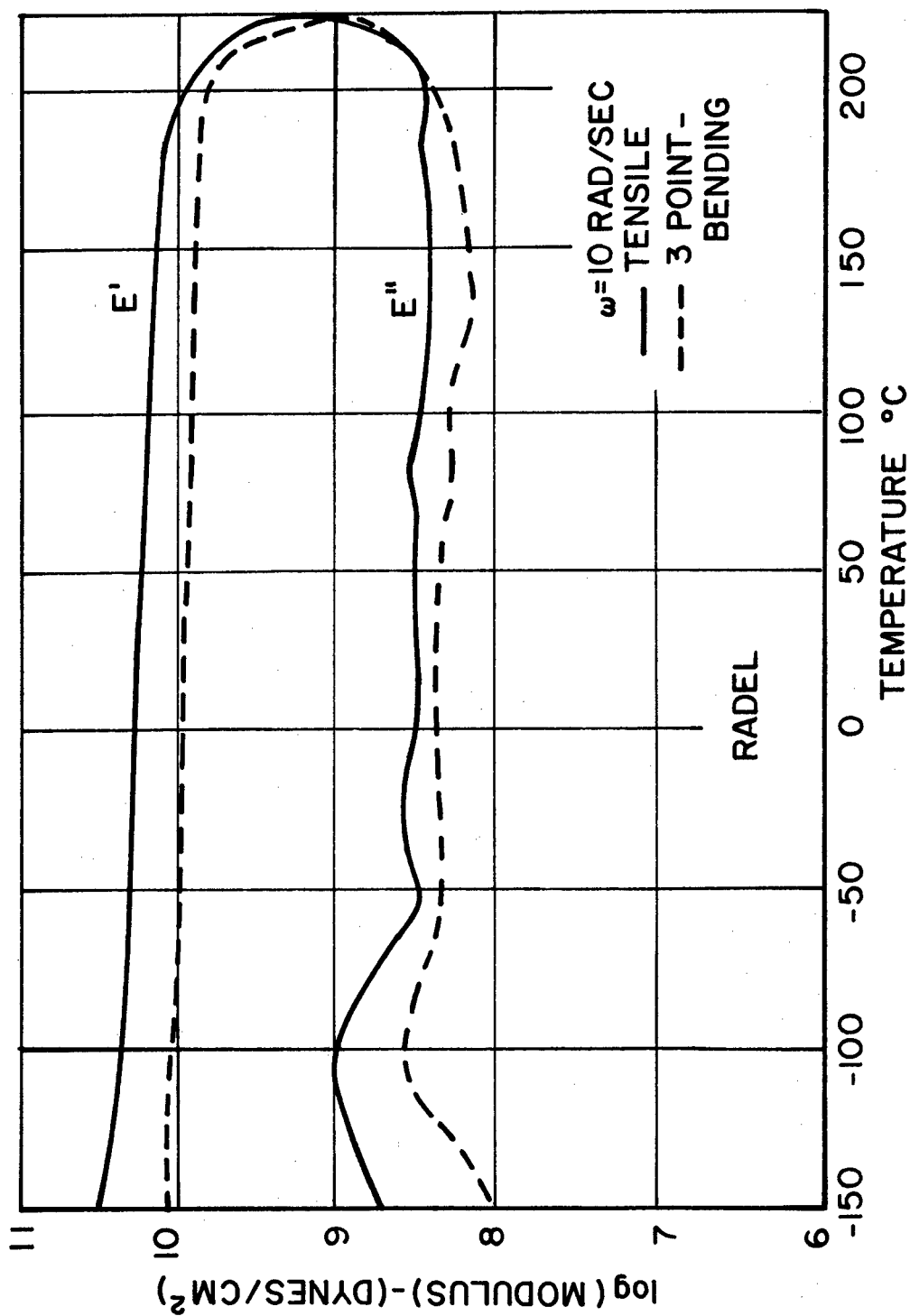


Figure 3. Tensile and 3-Point Bending (E' and E'') Results as a Function of Temperature.

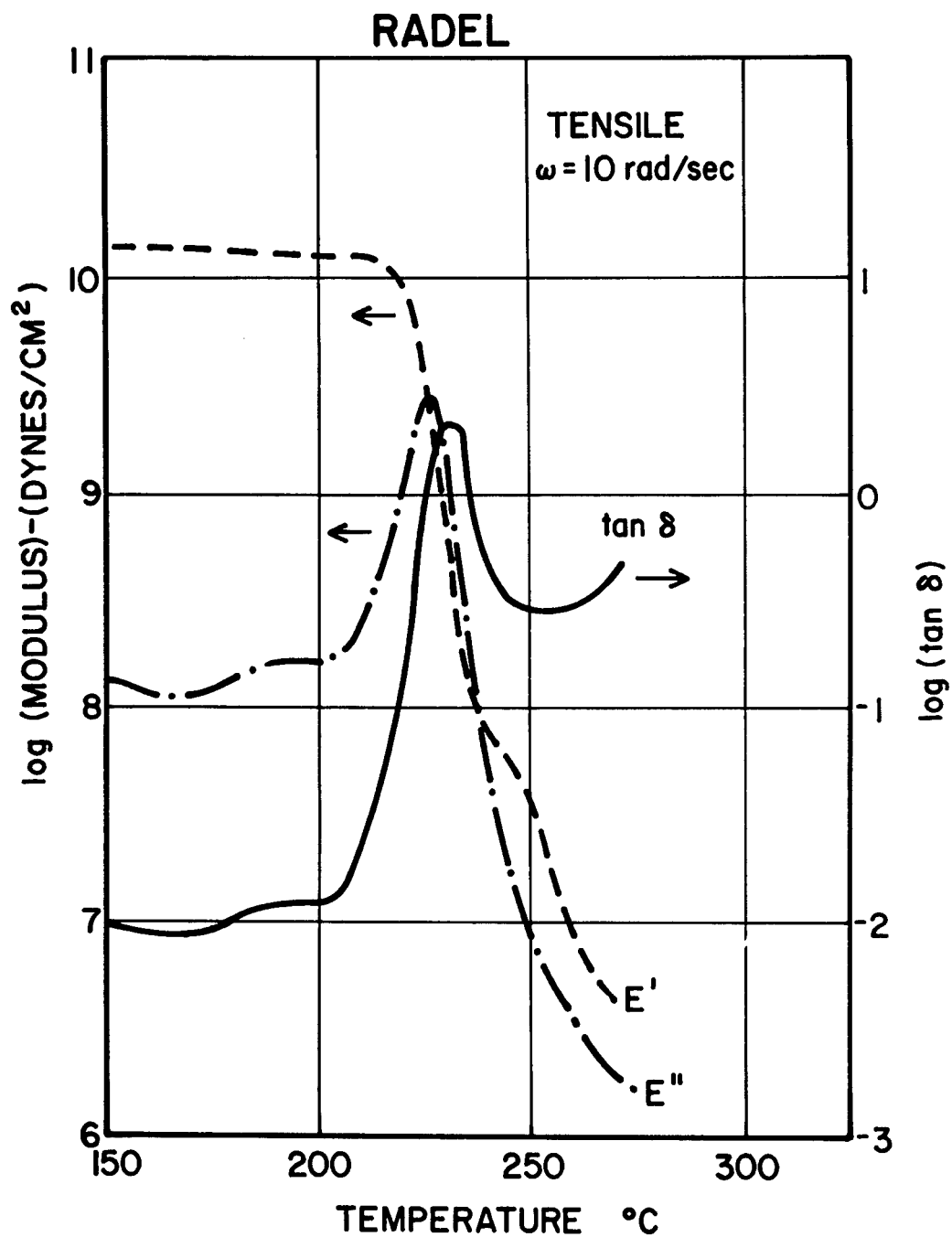


Figure 4. Tensile Result at the Glass Transition Region.

with the dynamic force. In order to accomodate the transient force, the Rheophaser has to be engaged in a higher input range, thus cutting down on the resolution of the dynamic force. There is also an upper limit to the dynamic force one can generate for measurement. To increase the dynamic force and to keep the specimen under tension, the transient force had to be increased. There was evidence of periodic slippage of the specimen if the tension were too high.

As a result, tensile experiments on the RMS are less reliable than torsion, and the resolution is also lower. The Radel results (Figure 3) show that the γ transition is detected in both 3 point-bending and tensile measurements, but the β transition is not. This discrepancy will be discussed further in a later section.

Because of all these limitations with the tensile mode, this mode of measurement is not recommended with RMS except in those cases where sample size limitation made torsional measurement impossible. The tensile modulus at room temperature is measured as 2×10^{10} dynes/cm², which yields a Poisson's ratio of about 0.3, as compared with 0.33 reported for polysulfone.⁽⁷⁾

PARALLEL PLATES

All the above measurements exhibit a lower limit of $10^6 - 10^7$ dynes/cm². Below this limit, polymers are usually in the flow region. The Parallel Plates measurement technique is suited for this region. Measurements have been made with this mode of measurement from 240°C to 380°C. The G' and G'' plots for 10 rad/sec are shown in Figure 5. Below 240°C, the sample was too rigid so the measurement was plagued by sample slippage. The result from the torsional experiment is also shown in Figure 5, and it can be seen that the two measurements agree well and complement each other to extend the range of measurement possible on a material.

RADEL - PAR. PLATES MEASUREMENT

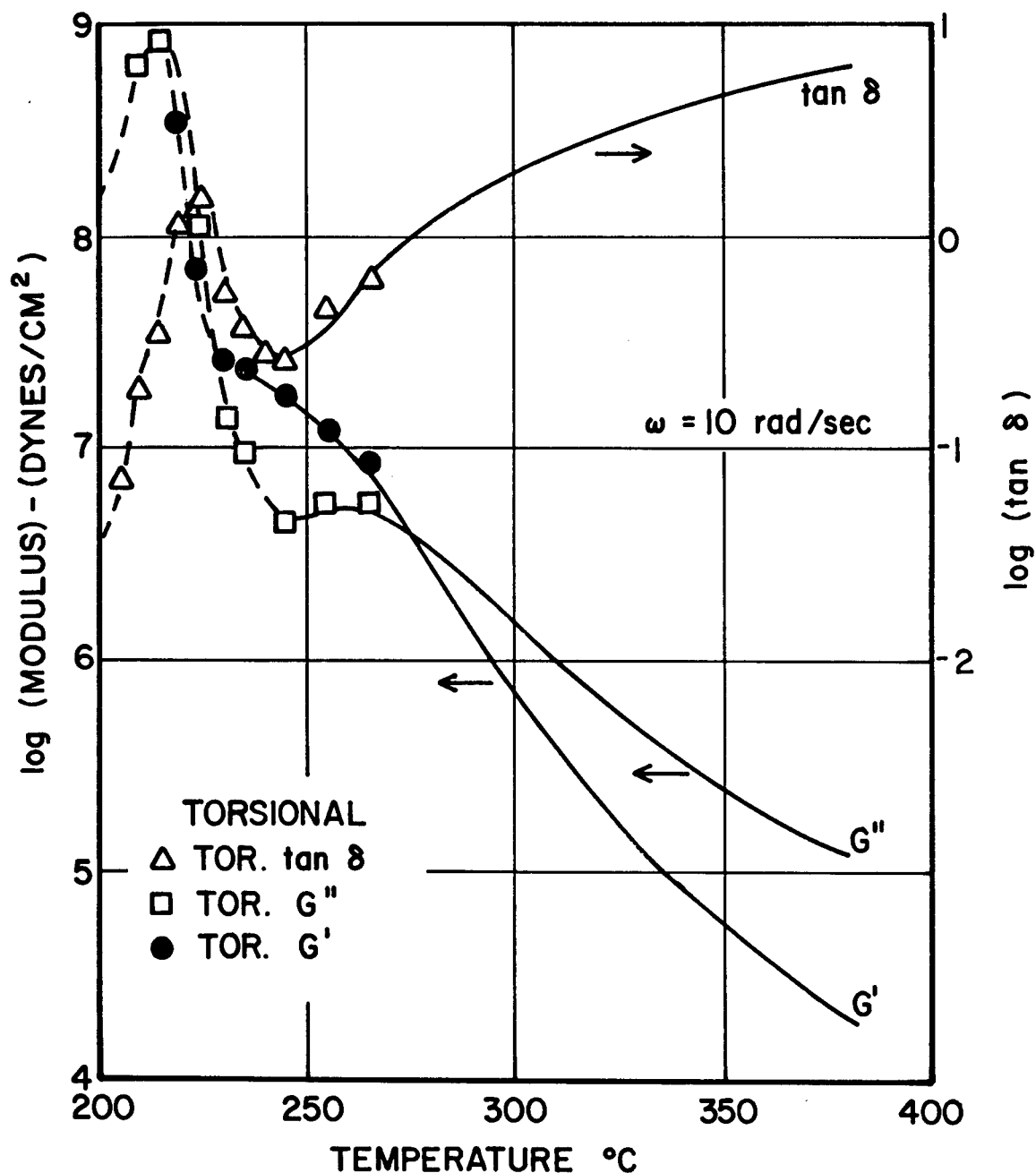


Figure 5. Parallel Plates Results (G' , G'' and $\tan \delta$) at Region above Glass Transition Temperature.

Figure 6 shows the $\tan \delta$ plot of the 4 frequencies used in this experiment. In this range of temperature, the two low frequency results indicate the presence of another peak after the T_g transition peak. The trend indicates the peak maxima for the two high frequencies are beyond 380°C . This transition corresponds with the $T_{\ell, \ell}$ transition proposed by Gillham.⁽⁴⁾ The G' and G'' results for $\omega = 0.1$ rad/sec are also shown in Figure 6. The G' curve indicates its value levels off after the $\tan \delta$ maximum at about 325°C . The $\tan \delta$ peak is then evidently associated with the transition of a polymer melt to the rubbery plateau. Whatever mechanism associated with the $T_{\ell, \ell}$ transition is also causing this rubbery transition to melt.

Figure 7 shows the viscosity plots of the four frequencies. One general observation that can be made is that the viscosity is highly non-Newtonian at low temperature. The viscosity values differ by 3 orders of magnitude with a difference of 3 decades in frequencies. At 380°C , they differ by only a factor of 3. It is not sure if this change in viscosity behavior can be related to the $T_{\ell, \ell}$ transition.

So far $T_{\ell, \ell}$ transition has been reported only for polystyrene, although there was some evidence suggesting the presence of another transition after the T_g transition for other polymers. Even for polystyrene, this $T_{\ell, \ell}$ transition is very evasive, being present in some measurements and not observed in others. There were some doubts about its existence⁽⁴⁾. The most supportive evidence so far is from Torsional Braid Analysis (TGA). This gives rise to speculations that this transition is actually an interaction between the polystyrene and the supporting braid during the measurement. The data presented here demonstrates the presence of another $\tan \delta$ maximum after T_g , and the evidence suggests this maximum is closely related to the flow region. Having demonstrated that Parallel Plates measurement can observe this $T_{\ell, \ell}$ transition, this phenomenon should be investigated further in the

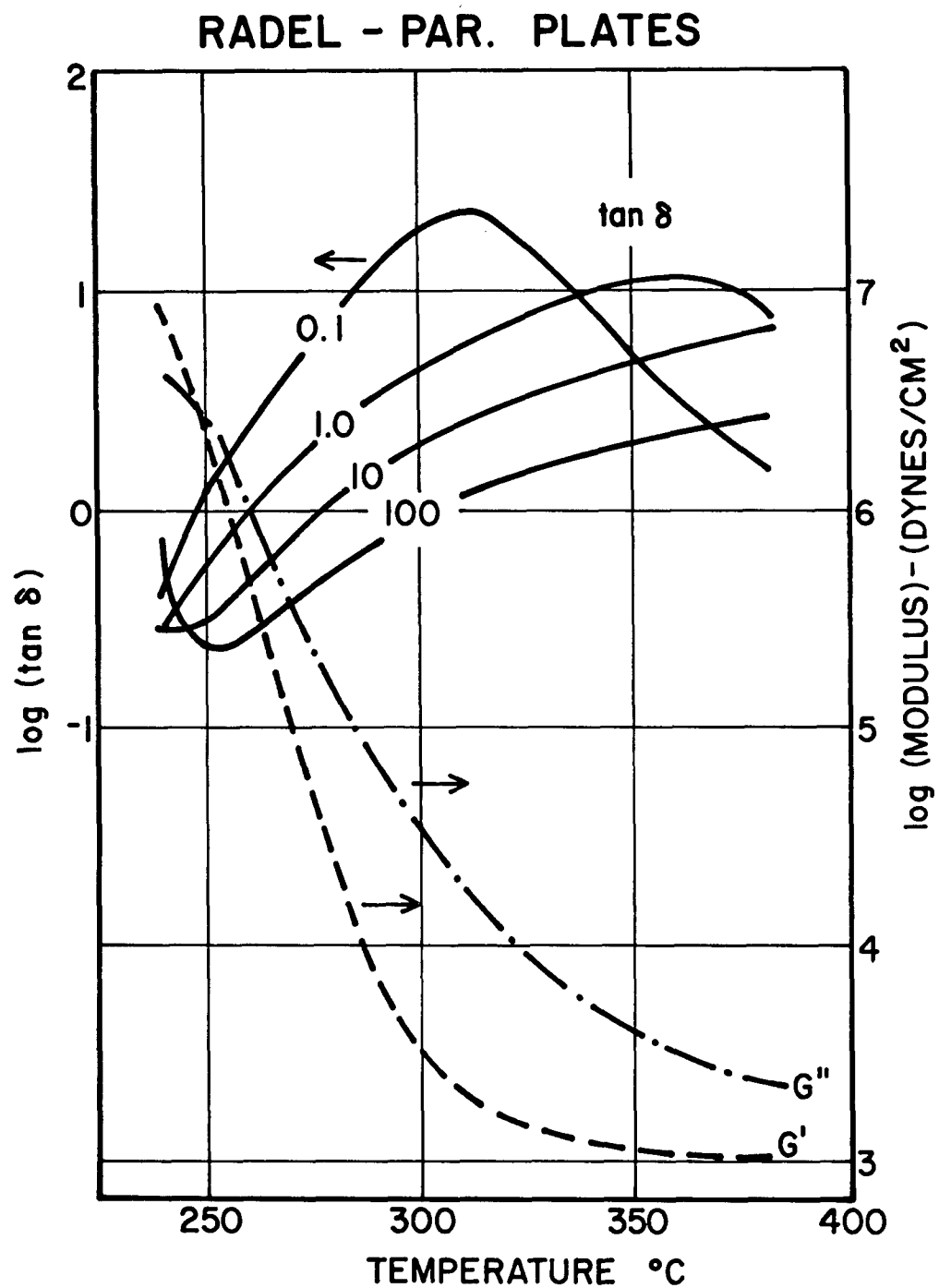


Figure 6. $\tan \delta$ Plots of Parallel Plates Measurement at Various Frequencies. The G' and G'' shown is for $\omega = 0.1$ rad/sec.

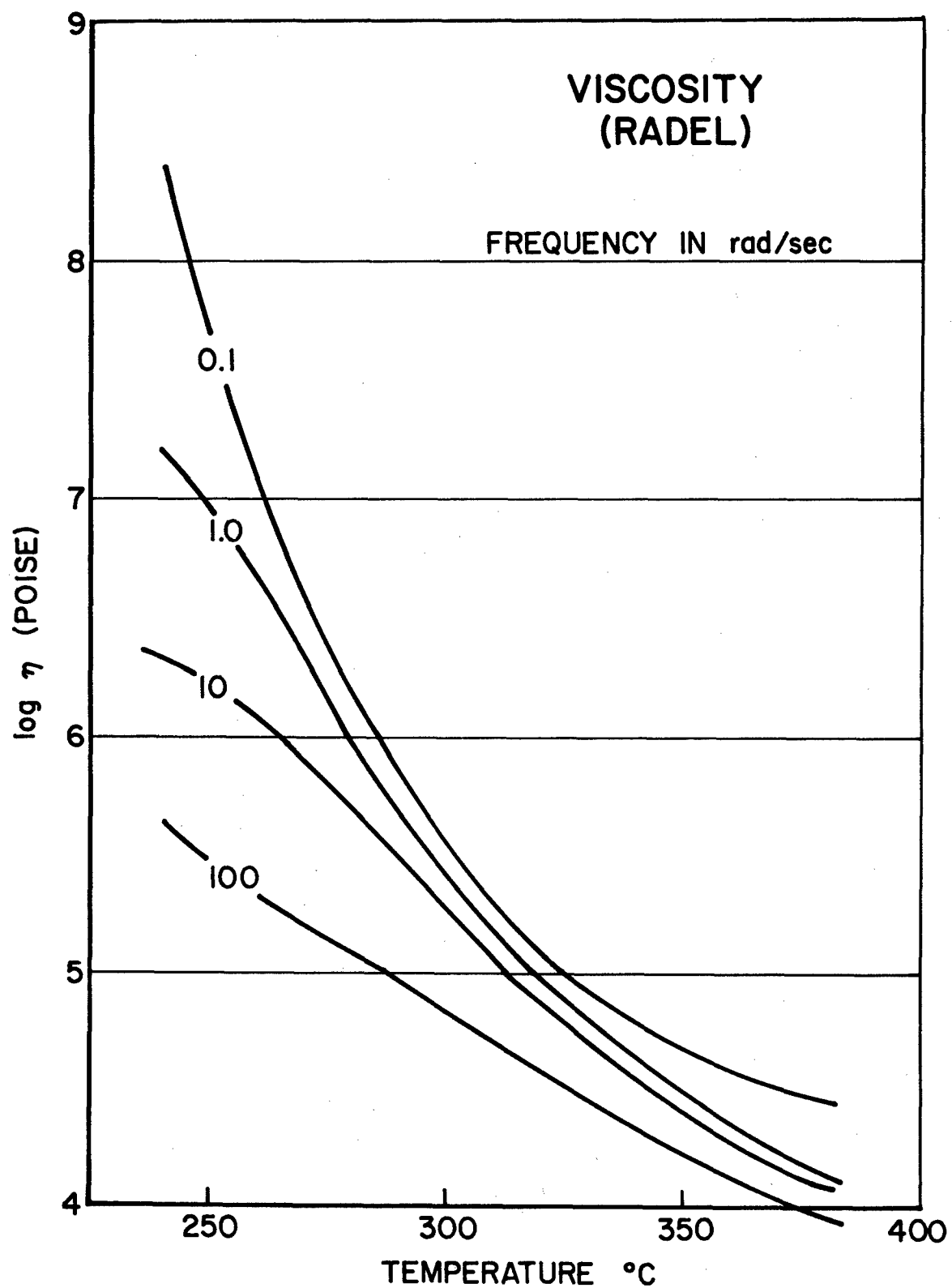


Figure 7. Plots of Parallel Plates Measurement at Various Frequencies.

future with this technique.⁽⁴⁾ It has been suggested that the processing temperature of thermoplastic should be above this transition temperature.

TRANSITIONS

Considering the combined data, a T_g transition, 2 glassy state transitions, and the $T_{\ell,\ell}$ transition can be identified. In this section, we will limit our discussion to the 2 glassy state transitions and the T_g transition.

Table 1 lists all the transition temperatures measured in different frequencies. For the β and γ transition, the G' changes very little through the transition region, so the $\tan \delta$ maximum and the G'' maximum are virtually at the same temperature. Such is not the case for the T_g transition, so both temperatures of $(\tan \delta)$ maximum and G'' maximum are reported.

For the β transition, only torsional data is available. For the T_g and γ transition, results from different modes of measurement are listed together. In general, there is good agreement between different modes of measurement. For the T_g transition, the values reported for the torsional experiment are lower than that from the tensile mode by a constant value. The $(\tan \delta)$ maxima have a difference of 8°C and the G'' maxima have a difference of 12°C . This difference can be explained by the temperature gradient that exists in the environmental chamber enclosing the test specimen. This gradient will depend on the flow rate of the gas used to regulate the temperature. The thermocouple recording the temperature is in the middle of the chamber, so the temperature recorded is always the maximum for temperatures above room temperature. Gaseous nitrogen was used as the temperature controlling agent in the experiment where the Tensile T_g data were obtained, while liquid nitrogen was used in all other experiments. The torsional experimental result is believed to be more reliable because of its good agreement with the

TABLE 1
TRANSITION TEMPERATURES^a
(Tan δ Maximum)

| | Torsion | Tensile | 3 Point-Bending |
|-------------------------------|------------------------|------------------------|-----------------|
| T_g Transition = rad/sec | | | |
| 0.1 | 215 (209) ^b | ---- | ---- |
| 1 | 220 (211) ^b | 228 (223) ^b | ---- |
| 10 | 224 (215) ^b | 231 (226) ^b | ---- |
| 100 | 229 (218) ^b | 237 (230) ^b | ---- |
| β Transition | | | |
| 0.1 | -5 | --- | ---- |
| 1 | 15 | --- | ---- |
| 10 | 32 | --- | ---- |
| 100 | 70 | --- | ---- |
| γ Transition | | | |
| 0.1 | -125 | --- | ---- |
| 1 | -113 | -120 | -112 |
| 10 | -108 | -105 | -102 |
| 100 | -93 | -95 | ---- |

^a All temperatures are in °C.

^b The values in bracket are the G" maximum temperatures.

Parallel Plates data whose temperature gradient is at a minimum because of the geometry of the test fixtures.

The shift of the ($\tan \delta$) maximum as a function of frequency is related to the activation energy involved in the transition (assuming Arrhenius type conditions hold) through the following equation (5)

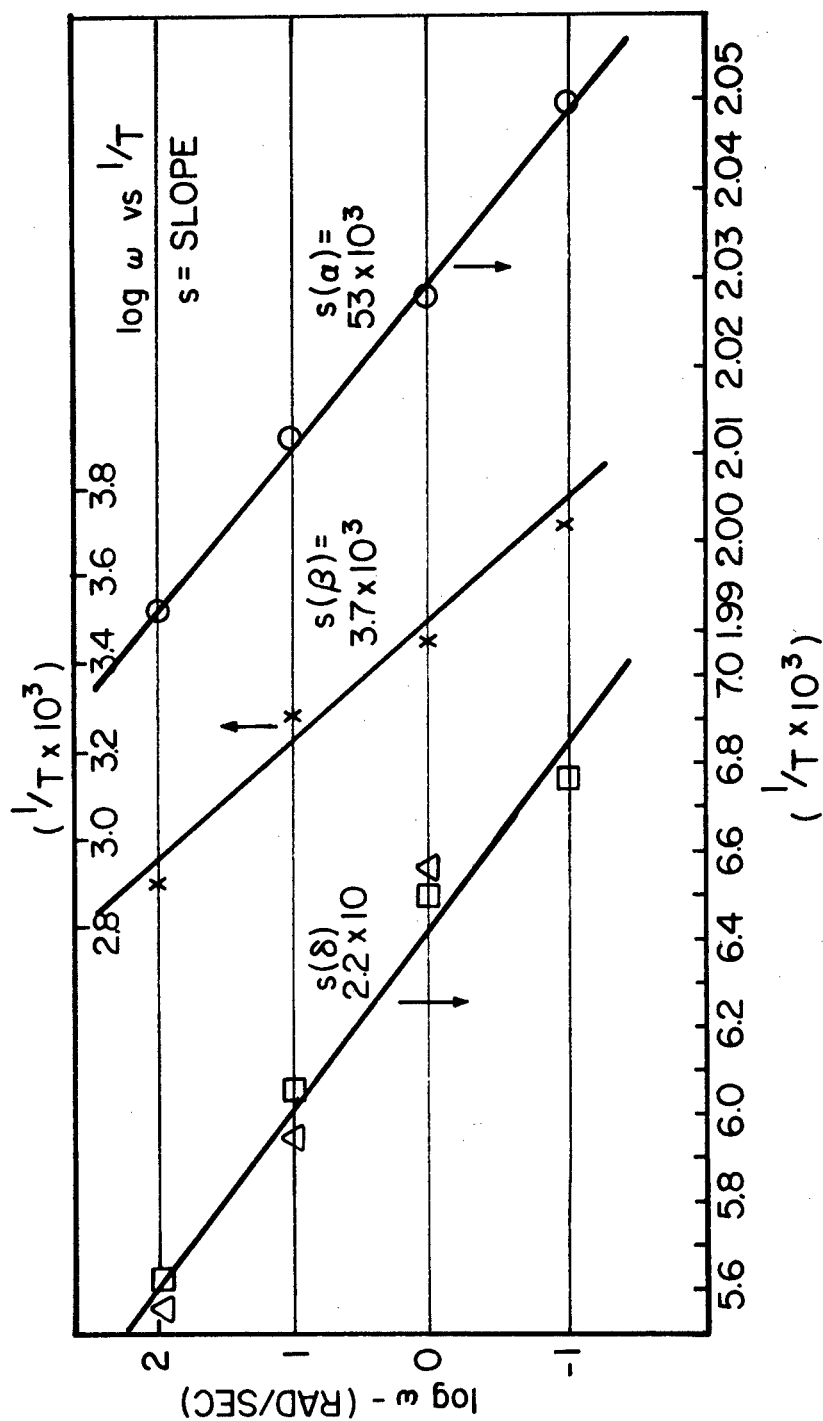
$$2.303 \log \omega = A \frac{\Delta H}{R} \left(\frac{1}{T} \right)$$

where ω is the frequency of measurement; A is a constant; R is the gas constant; T is the temperature of the ($\tan \delta$) maximum;

ΔH is the activation energy. Figure 8 is a plot of the $\log \omega$ vs. $1/T$ for the different transitions. All sets of data show a linear relationship, agreeing with the equation above. From the slopes, the ΔH values are calculated to be : glass transition = 243 kcal/mole, β transition = 17 kcal/mole, and γ transition = 10 kcal/mole.

The γ transition at about -100°C has in many cases been associated with the presence of moisture. (6) The data from Union Carbide indicates the transition of the peak is present even when the sample is dry. With moisture, this loss peak just becomes more prominent. Assuming the sample is indeed dry, the transition must be associated with molecular motion of the molecule, which accidentally is at the same region as the moisture peak on the temperature scale. One possible candidate is the rotation of the p-benzene ring found in the Radel monomer repeat unit. Since there are no pendant groups in Radel, this transition must be due to rotation of elements on the backbone.

It has been found that the glass transitions and glassy state transitions ($\text{sub-}T_g$) can be characterized by the dimensionless quantity (8)



$$\Delta T^* = \frac{T(10 \omega_0) - T(\omega_0)}{T(\omega_0)}$$

$$= \frac{2.303 RT(10 \omega_0)}{\Delta H}$$

where $T(\omega_0)$ and $T(10 \omega_0)$ are the temperatures of the loss ($\tan \delta$) maximum with frequency ω_0 and $10\omega_0$, respectively, and ΔH is the activation energy of that particular transition. For a reference frequency of 1 Hz, the glass transitions have as ΔT^* values of about 0.01, while the sub- T_g transitions about 0.07, regardless of the chemical structure of the polymers. For Radel, a value of 0.0092 was calculated for the glass transition and values of 0.093 and 0.082 respectively for the β and γ transitions, in good agreement with the general values.

For all the data used in this work, the β transition shows up only in the torsional experiment and the result released by Union Carbide. Lack of sufficient sensitivity in the other experiments could be a reason, but this is not really a convincing argument. The other measurements are all in the tensile mode, but it is difficult to conceive a mechanical transition that will show up only in torsion. Heijboer⁽⁹⁾ had reported two transitions in the glassy state for polysulfone, one at -100°C and the other at 60°C , very similar to the two transitions observed for Radel. His work indicated the transition at 60°C can be suppressed by certain processing conditions of the test specimens. In retrospect, insufficient processing conditions have been recorded to distinguish the difference between the torsional specimen from the others, so it is not appropriate to say if the result is in agreement with Heijboer's observation. However, since this transition behaves exactly like a glassy transition, it will be treated as one for the time being regardless of its origin. This point can only be clarified by further investigation.

The Rheovibron result also shows the γ transition, but the maximum is at -85°C . The frequency used was 11 Hz (69 rad/sec). According to the results obtained with the RMS, the

maximum should occur at about -95°C . The discrepancy can again be explained by the lack of good temperature control in the Rheovibron sample chamber, so the recorded temperature actually is higher or lower than the sample temperature depending on whether the temperature in question is above or below the room temperature. This explanation is consistent with the higher transition temperature observed in the Rheovibron results.

MASTER CURVE

One of the nice features of the RMS is the ability to hold the sample temperature at a constant value and perform a frequency sweep covering 3 decades in range. This makes the construction of a master curve relatively easy. Results from the torsional and the parallel plates experiments are used here for such a construction because they agree with each other, and together will cover a much wider range beyond T_g .

Since frequency temperature superposition supposedly works only for region close to or above T_g , the lowest temperature used was 201°C . The curve was extended well into the flow region. Figure 9 is the composite plot of G' , G'' and $\tan \delta$. The reference temperature used in the plot is 240°C , the overlapping temperature of the two measurements. The curve starts from the glassy region at the highest frequency end and passes thru the transition region onto a rubbery plateau; it then goes through another transition and seems to come to another plateau at the low frequency end.

In general the G' and G'' can be broken down into two parts:

$$G' = G_0 \psi'(\tau, \omega)$$

$$G'' = G_0 \psi''(\tau, \omega)$$

The numerical constant G_0 is dependent on the geometry and thermodynamic changes. The second part, ψ , is frequency dependent and is a result of the relaxation process. The former part will give

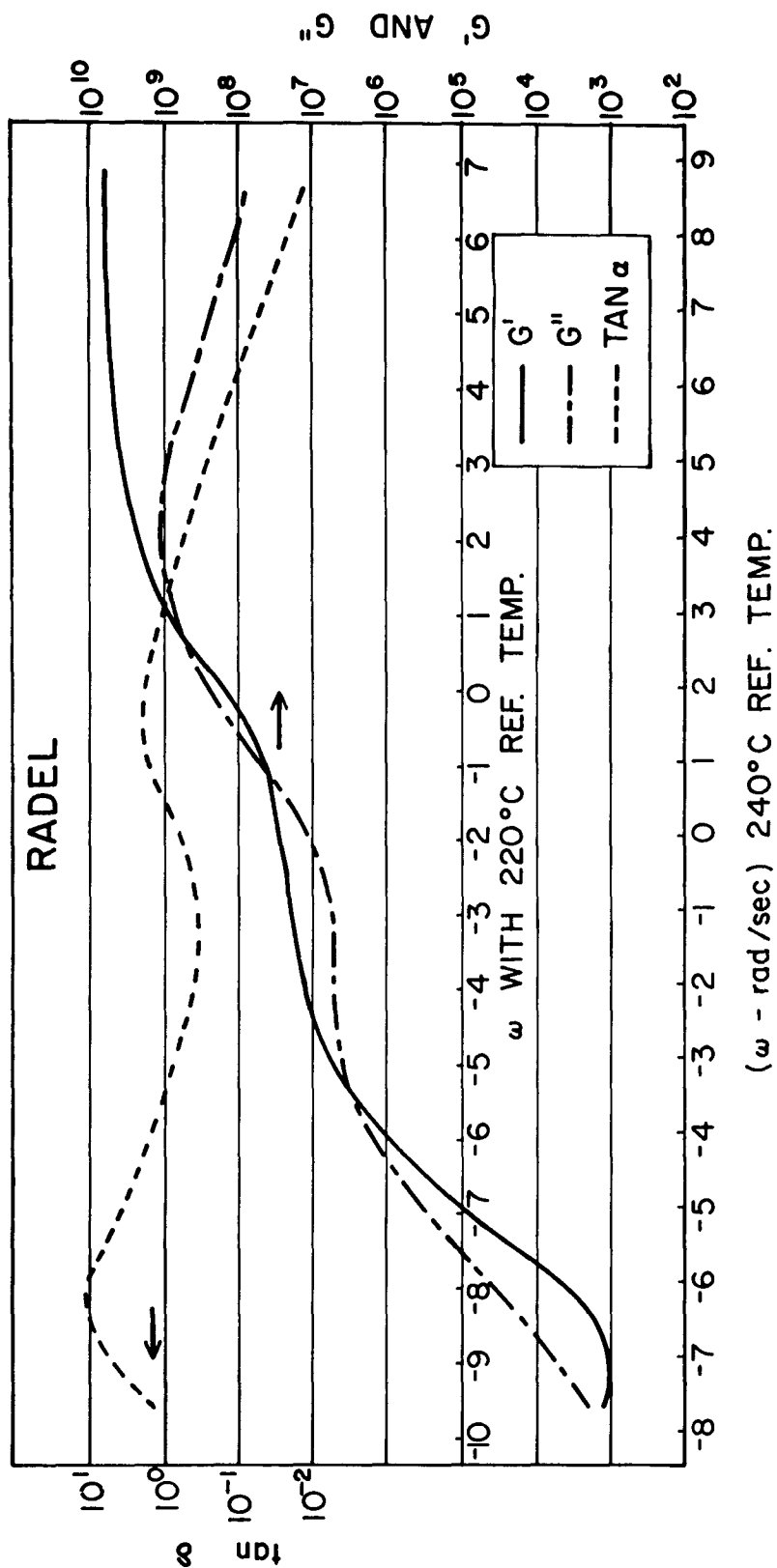


Figure 9. Master Curves (G' , G'' and $\tan \delta$) of Radel

a vertical shift, while the later part a horizontal shift when one tries to superpose G' or G'' curves from two different temperatures. For $\tan \delta$ curves, however, no vertical shifts are necessary since any changes required between the two temperatures cancel out. The vertical shift is small but not negligible. The horizontal shift is the shift in frequency and has been found to be governed in most materials by equation ⁽¹⁾

$$\log a_T = \frac{-C_1^0 (T-T_0)}{(C_2^0 + T-T_0)}$$

where $\log a_T$ is the log of the frequency shift, T is the temperature shifted and T_0 is the reference temperature. This equation is the Williams, Landel and Ferry (WLF) equation. The equation can be rewritten as:

$$\frac{(T-T_0)}{\log a_T} = - \frac{C_2^0}{C_1^0} - \frac{(T-T_0)}{C_1^0}$$

So a plot of $(T-T_0)/\log a_T$ vs. $(T-T_0)$ should be a straight line. Figure 10 is such a plot, and the data follows the WLF equation well. From the slope and the intercept, the C_1^0 and C_2^0 values for 240°C are calculated to be 6.80 and 51.0 respectively.

Choosing 220°C as the T_g of Radcl, one can calculate the C_1 and C_2 values at 220°C if this temperature has been chosen instead as the reference temperature in the construction of the master curve. Using the equations given in reference 1, the values at 220°C are calculated to be 11.2 and 31.0 respectively for C_1 and C_2 . These values compare well with the constants found with other polymers.

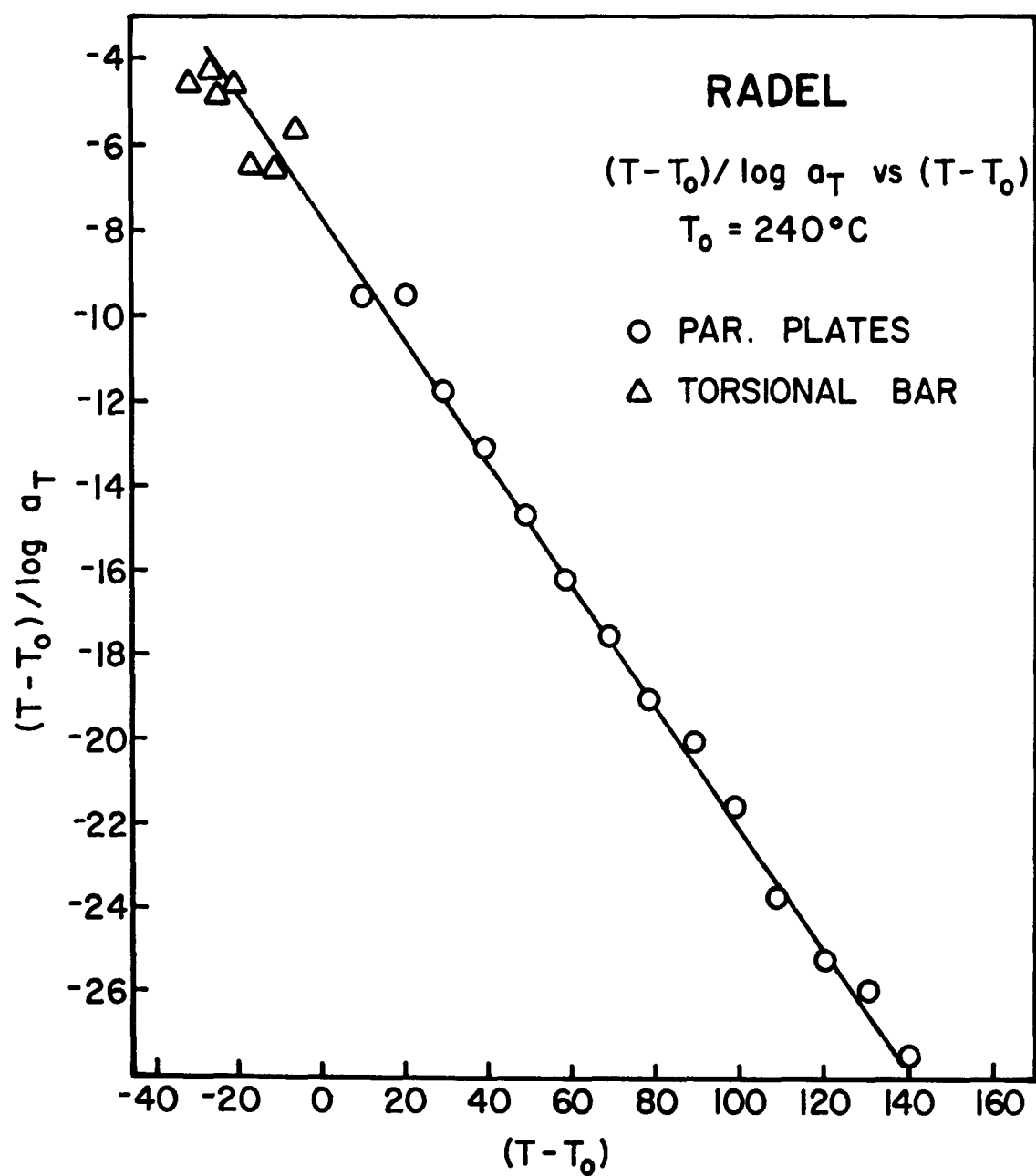


Figure 10. Fitting of $\log a_T$ According to the WLF Equation with Reference Temperature of 240°C .

SECTION IV

CONCLUSION

The results and their discussions have been covered in detail in the previous section. They are briefly summarized as follows:

- (1) The RMS results agree well with the results provided by Union Carbide. In general, the torsional measurement is more reliable and also will provide better resolution than the tensile measurement on this instrument.
- (2) The $T_{\ell, \ell}$ transition, the transition above the glass transition temperature, has been observed. Melt viscosity has been measured at temperatures above T_g . It is found to be highly non-Newtonian at low temperatures and progressively less so with increasing temperature.
- (3) The T_g was measured to be 220°C (at $\omega = 1.0$ rad/sec). Two sub- T_g transitions were observed (room temperature and about -100°C). The T_g and the low temperature transitions were observed in all modes of measurements, but not the transition at room temperature. Heijboer ⁽⁹⁾ had observed similar behavior before with polysulfone. It is not conclusive at this point if the observation in this work is the same phenomenon.
- (4) Activation energy for the three transitions are calculated to be $\Delta H(\alpha) = 243$ kcal/mole, $\Delta H(\beta) = 17$ kcal/mole, and $\Delta H(\gamma) = 10$ kcal/mole. The quantity ΔT^* has been calculated for the transitions as $\Delta T^*(\gamma) = 0.0092$, $\Delta T^*(\beta) = 0.093$, and $\Delta T^*(\alpha) = 0.082$, in good agreement with those reported for other polymers.
- (5) A master curve has been constructed. The data extended thru the flow region to approach a melt plateau. The shift parameters $\log a_T$ follow the WLF equation relationship nicely and yield C_1 and C_2 values at 220°C to be 11.2 and 31.0 respectively, in good agreement with values reported for other polymers.

In conclusion, the β transition of Radel and the $T_{\ell, \ell}$ transition phenomenon merit further investigation in the future. The transitions below T_g have been found in some cases to correlate with the impact strength ⁽¹⁰⁾ of the material. The β transition disappearance under certain conditions may have effects on the end use properties of the material. The $T_{\ell, \ell}$ phenomenon is not only of theoretical interest, it may have practical use for determination of processing parameters. The master curve obtained in this report is expected to be very helpful in the future improvement of the regularization method to obtain relaxation spectrum. So far this is the only master curve we are aware of that is extended well into the flow region. In reference to the chemical structure mechanical properties correlation program, it seems appropriate to fully characterize the dynamic mechanical response of polysulfone (Udel) in the future, since the structure of Udel is very similar to that of Radel.

TENSION AND COMPRESSION FIXTURE

PROGRAM 16 (E' , E'' , $\tan \delta$)

DYNAMIC - FORCED TENSILE OSCILLATION

$$\gamma_0 = \frac{\Delta L}{L} \times 100$$

$$\Delta L = \frac{0.254}{2\pi} \theta_0$$

$$E' = \frac{Fz}{\theta_0} \cos \delta \times 49.48 \times \frac{L}{WT} \times 980.7$$

$$= a \times 10^4 \times 49.48 \times \frac{L}{WT} \times 980.7$$

$$E'' = \frac{Fz}{\theta_0} \sin \delta \times 49.48 \times \frac{L}{WT} \times 980.7$$

$$= b \times 10^4 \times 49.48 \times \frac{L}{WT} \times 980.7$$

$$E^* = \sqrt{E'^2 + E''^2}$$

$$\tan \delta = E''/E'$$

where γ_0 = maximum strain amplitude, %

ΔL = maximum tensile oscillation amplitude, cm

L = sample length, cm

θ_0 = maximum motor oscillation amplitude, rad.

W = sample width, cm

T = sample thickness, cm

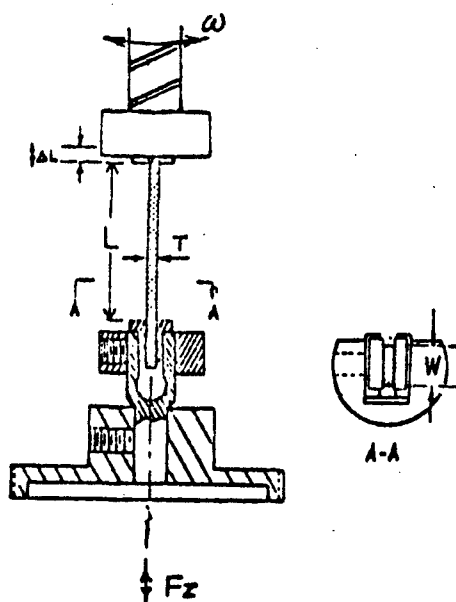
E' = tensile storage modulus, dynes/cm²

δ = phase angle, degrees

a = "a" value from Rheophaser

b = "b" value from Rheophaser

Fz = maximum tensile oscillation force amplitude, gr



APPENDIX

EQUATIONS FOR CONVERTING TORQUE SIGNALS TO MODULUS AND VISCOSITY

RECTANGULAR TORSION FIXTURE

PROGRAM 13 (G' , G'' , $\tan \delta$)

DYNAMIC - FORCED TORSION OSCILLATION

$$\gamma_0 = \frac{T\theta_0}{L} \times 100$$

$$\theta_0 = V/0.14$$

$$G' = \frac{M_0}{\theta_0} \cos \delta \times \frac{16L \times 980.7}{\pi T^3 (16/3 - 3.36 T/W)}$$

$$= a \times 10^4 \times \frac{16L \times 980.7}{\pi T^3 (16/3 - 3.36 T/W)}$$

$$G'' = \frac{M_0}{\theta_0} \sin \delta \times \frac{16L \times 980.7}{\pi T^3 (16/3 - 3.36 T/W)}$$

$$= b \times 10^4 \times \frac{16L \times 980.7}{\pi T^3 (16/3 - 3.36 T/W)}$$

$$G^* = \sqrt{G'^2 + G''^2}$$

$$\tan \delta = G''/G'$$

where γ_0 = maximum strain amplitude, %

T = sample thickness, cm

L = sample length, cm

W = sample width, cm

θ_0 = maximum angular oscillation amplitude, radian

V = volt output from Rheophaser

G' = storage modulus, dynes/cm²

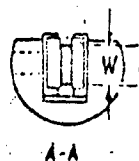
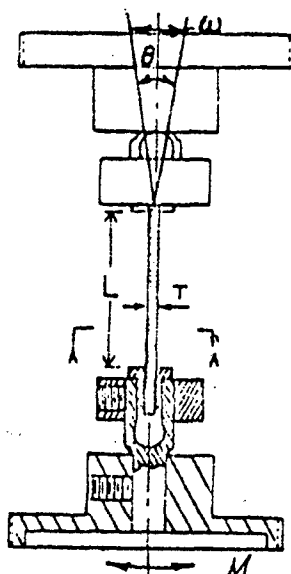
G'' = loss modulus, dynes/cm²

G^* = complex modulus, dynes/cm²

a = "a" value from Rheophaser

b = "b" value from Rheophaser

δ = phase angle, degree



PARALLEL PLATES

PROGRAM #5 (G' , G'' , $\tan \delta$)
and #7 (G' , G'' , η^*)

DYNAMIC - SINUSOIDAL OSCILLATION

$$Y_0 = \frac{R\omega_0}{h} \times 100$$

$$\theta_0 = V \times 0.14$$

$$G' = \frac{M_0}{\theta_0} \cos \delta \times \frac{2h}{\pi R} \times 980.7$$

$$= a \times 10^5 \times \frac{2h}{\pi R} \times 980.7$$

$$G'' = \frac{M_0}{\theta_0} \sin \delta \times \frac{2h}{\pi R} \times 980.7$$

$$= b \times 10^5 \times \frac{2h}{\pi R} \times 980.7$$

$$\eta^* = \frac{\sqrt{G'^2 + G''^2}}{\omega}$$

$$\tan \delta = G''/G'$$

where Y_0 = maximum strain amplitude, %
 θ_0 = maximum angular oscillation amplitude, radian
 R = radius of the cone, cm
 h = sample thickness, cm
 V = volt output from Rheophaser
 M_0 = maximum torque amplitude, gr-cm
 G' = storage modulus, dynes/cm²
 G'' = loss modulus, dynes/cm²
 a = "a" value from Rheophaser
 b = "b" value from Rheophaser
 η^* = dynamic viscosity, poise
 ω = frequency, rad/sec
 δ = phase angle, degree

